

Fabrication and Properties of Lignin Based Carbon Nanofiber

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Abstract

Lignin, the second most abundant biopolymer on earth, has the potential as a low cost and renewable precursor for carbon fibers. By creating lignin carbon nanofibers for lightweight structural composites for automobiles and functional applications as electromagnetic shields, the value of lignin will be enhanced. Under the Lignoworks Biomaterials and Chemicals Network program, we demonstrated the feasibility of producing carbon nanofibers from softwood Kraft lignin by electrospinning and heat treatment. The morphological, mechanical, and electromagnetic properties of the lignin carbon nanofiber were characterized. Results showed 10 times increase in strength for the lignin random nanofiber mats after carbonization. Alignment of fibers further improved the mechanical strength. By doping the lignin polymer with carbon nanotubes and functional nanoparticles such as magnetite, we demonstrated the feasibility of translating the strength and electromagnetic function respectively to the lignin nanofiber assemblies. The encouraging results demonstrated the potential of lignin as an engineering material thus establishing a pathway for adding values to the abundantly available lignin.

Keywords: Lignin; Carbon Nanofiber; Mechanical Properties; Multifunctional Nanofiber

1 Introduction

The increasing global energy demand and its consequential impact on the environment have prompted interest in renewable resources as feedstock for the manufacturing of value added products. Amongst the renewable materials lignin is relatively unexplored but holds great potential. Lignin is the second most abundant biopolymer on earth only after cellulose and is one of the three main constituents in trees [1-4]. Lignin varies with wood species as well as the process to isolate it. In softwood, lignin represents about 30% of the total mass, whereas lignin constitutes 20-25% in hardwood [3-6]. Native lignin is made up by peroxidase-mediated dehydrogenation of three types of phenyl propane monomer units (monolignols) and linked by carbon-carbon and aryl-ether linkages with random cross-linked polymerization from radical-coupling reactions between phenolic radicals [2-3]. The monomer units can be classified into three different types: guaiacyl, syringyl, and 4-hydroxyl-phenyl propane structures [2]. There are several different C-O

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Lignin is a byproduct of pulp and paper industry as well as cellulosic ethanol fuel production (Fig. 2 [7]). In the pulp and paper industry, Kraft pulping is the most dominant chemical pulping process in the world generating over 68 million tons of lignin yearly [3]. In Kraft pulping, a solution of sodium hydroxide (NaOH) and sodium sulfide (Na_2S) is used to dissolve most of lignin in a temperature range of 155-175 °C for several hours. The resulting solution is called black liquid that can be separated from cellulose [3-4]. After Kraft pulping, the lignin solution can be concentrated and recovered to a dark brown powder. Kraft lignin is hydrophobic and its molecular mass is lower than the native lignin [3]. It is important to note that the large amount of lignin produced during pulping process, less than 2% of the lignin is applied for commercial products such as dispersants, adhesives, and surfactants [5]. Most of lignin is burned as fuel after recovery and the value of fuel is low (400 \$/tonne). Accordingly there are great interests in

turning lignin into other product forms that would add value to lignin. Because of the potential to serve as low cost precursor for carbon fibers, it has been identified that lignin in carbon fiber form has the highest potential to add significant value to lignin (21 680-800 000 \$/tonne) [8-9].

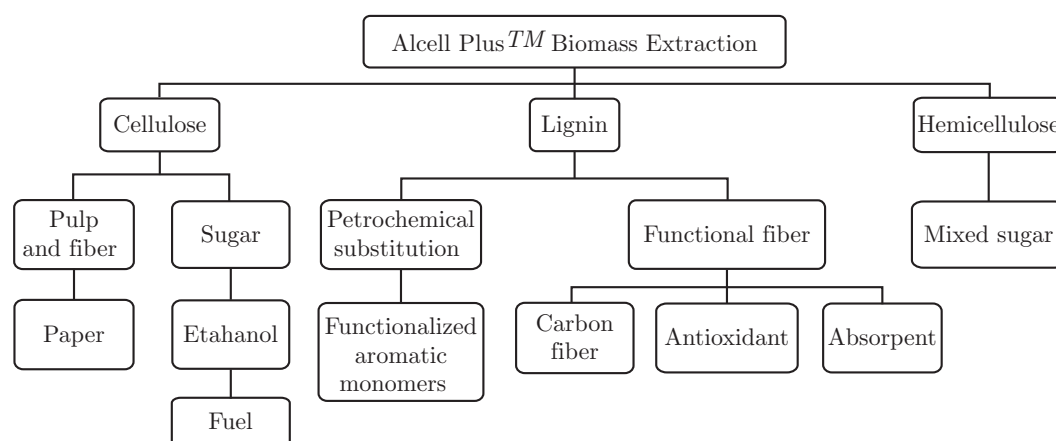


Fig. 2: Biorefinery process at Lignol [7]

Lignin in carbon fiber form can add value to lignin by serving as structural reinforcement for lightweight composites and by serving as a carrier for special functions. Demand for carbon fibers, as lightweight structural materials, has been found in numerous industries, such as aerospace, automotive, sport equipment and other consumer products. Carbon fibers are also burgeoning in electrical and electronics industry and the energy storage area. Typical applications include brush contact in commutator brush, position sensor, switches and static discharge eliminator devices, electrodes in capacitors and batteries, and electromagnetic interference shields [10]. Global market of carbon fiber has exponential growth in recent years and the estimated demand of carbon fiber could reach to 70 000 tonnes/year in 2015 at the 10-15% growth rate [11-12]. Besides, the whole global estimated market value of carbon fiber is \$7.3 billion/year by 2017 [12]. Currently about 95% of carbon fiber precursors are made from polyacrylonitrile (PAN), which is a petroleum-based material [13]. Due to the high processing costs of PAN, the expansion of carbon fiber applications remains limited to high-end specialty products. In 2010, the PAN-based carbon fiber manufacturing cost was around \$9.88/lb, and the precursor cost of PAN based carbon fiber was over 50%. If the precursor is replaced by lignin, the carbon fiber cost could be reduced to \$3.71/lb. Therefore; lignin is an excellent candidate as a low cost precursor for carbon fiber. In principle, to form high performance carbon fiber, a randomly oriented melted (like isotropic pitch) or solutions of linear polymers (like PAN) must be converted to as-spun fiber having a high degree of preferred molecular orientation along fiber axis. The structural transformation achieved during spinning and drawing entails a number of complex molecular processes. Subsequently, the as-spun polymeric fibers are converted to carbon fiber under heat treatment. In this process, some factors involved are time and temperature dependent molecular motion, crystallization, and phase transition under tension, chain entanglement constraints, and various chain and inter-chain reactions [13]. However, differ from pitch and PAN, lignin has 3-D heterogeneous chemical structure. It is quite challenging to obtain high performance carbon fiber from lignin.

Lignin-based carbon fiber has been previously reported. The first lignin-based carbon fiber made by Otani *et al.* [14]. However, the sodium impurities caused micro voids, which resulted in low modulus and low tensile strength. Lignin carbon fiber could also be produced by blending with biopolymers. Kadla *et al.* produced carbon fibers from Hardwood Kraft Lignin (HKL)

blended with poly (ethylene oxide) (PEO) [1]. Their research showed that PEO was miscible with the lignin and could enhance the fiber melt spinning ability. The tensile strength and the modulus were in the range of 0.40–0.55 GPa and 30–60 GPa, respectively. Kubo and Kadla further produced carbon fibers by blending HKL with poly (ethylene terephthalate) (PET) [2]. At a HKL/PET ratio of 75/25, the tensile strength and modulus were increased to 0.7 GPa and 94 GPa, respectively. Recently the Oak Ridge National Laboratory (ORNL) in the United States also manufactured lignin-based carbon fiber and the average strength and Young's modulus could reach to 1.07 GPa and 82.7 GPa, respectively [13]. Nevertheless the tensile strength of lignin carbon fibers is relatively low comparing to commercial PAN-based carbon fiber (3–7 GPa). It is well known that the strength of fibers can be improved by reducing the fiber diameter. Electrospinning is an effective method to generate nano- to micro- scale fibers. The nanofiber has unique properties such as high specific surface area and superior directional strength, and could be used for many applications ranging from tissue engineering to composite reinforcements [15–18]. Over the past decade, enormous studies and a variety of polymers were used to generate electrospun fibers [16]. Through electrospinning, nanofibers or nanoparticle-filled nanofibers can be obtained from the polymer solutions or nanoparticle polymer suspensions. These fibers can be subsequently fabricated into yarns, fabrics, and composites for a wide range of applications [12].

Under the Lignoworks Network program we work closely with the Canadian forestry industry to develop the next generation of low cost value added lignin based carbon nanofiber. The lignin was converted into nanofiber form by electrospinning method and subsequently carbonized into carbon nanofiber [19–20]. The mechanical properties of single as-spun nanofiber as well as carbon nanofiber mats were examined. Randomly distributed and aligned electrospun lignin nanofiber mats were collected and tested to investigate the mechanical strength improvement by alignment. Another way to add value to lignin is to add functions to the carbon nanofibers. The general process for preparing multifunctional nanofiber is to combine nanoparticles of various geometries and properties with a suitable polymer matrix by co-electrospinning to form composite nanofibers [20–21]. Various multifunctional composite nanofibers have been produced in our lab and the preliminary results are encouraging. These multifunctional composite nanofibers can be used in different applications. For example, in structural composites, carbon nanotubes (CNT) reinforced PAN nanocomposite fibers have been fabricated [22]. It was shown that co-electrospinning provided an excellent means for the translation of the mechanical properties of CNT to polymer fibril matrix by the inclusion of a small amount of CNT. Multifunctional composite nanofibers can also be used in electrical and electronic applications. Electromagnetic nanofibers have been developed through the incorporation of magnetic nanoparticles to PAN by electrospinning [23]. Lithium ion battery anode has been prepared by electrospinning of poly (acrylonitrile-co-acrylamide) (PANAM) and silicon nanoparticles [24]. Using the process of electrospinning, nanofiber materials as a transparent conductor have been developed and their performance for applications in solar cell has been explored [25]. In biomedical applications, electrospun Ag/PLLA fibrous membrane has been used as an antibacterial scaffold for tissue engineering [26]. It is quite evident that multifunctional composite nanofibers are promising means to transfer functions from nanoparticles to polymer and thus enhancing the performance of materials.

In this paper the various ways to increase the strength of lignin fiber were examined. We further illustrated the concept of lignin based multifunctional composite fiber. By combining the electrical conductive function with magnetic function the composite lignin carbon nanofiber was shown to be electromagnetic active.

2 Experimental

Softwood Kraft Lignin (SKL) was fractionated to extract specific fractions, 4th fractionation (F₄SKL), with proper molecular weight and molecular weight distribution. F₄SKL was electrospun into nanofiber, and then thermal-stabilized and carbonized into carbon nanofibers. Magnetic nanoparticles were added to lignin carbon nanofiber by in-situ synthesize method.

2.1 Materials

SKL (Indulin-AT) was purchased from Meadwestvaco (Glen Allen, VA, USA). PEO (Mw = 1×10^6 g/mol) was obtained from Sigma-Aldrich. Iron (III) acetylacetonate (AAI) was purchased from Sigma-Aldrich. N, N-dimethylformamide (DMF), methanol, and methylene chloride were all ACS Reagent grade and obtained from Fisher Scientific (Ottawa, ON).

2.2 Methods

2.2.1 Lignin Fractionation

SKL is a poly-disperse mixture of lignin fragments with a variety of chemical structures. Fractionation is required to divide SKL into more discrete, less heterogeneous fractions. Commercially available SKL was divided into fractions by successive extraction with organic solvents, based on the previously reported process [19]. SKL was washed with hydrochloric acid (pH = 2) and subsequently washed with organic solvents, including methanol and mixed methanol/dichloromethane. The 1st, 2nd and 3rd fractionation (F_{1–3}SKL) and 4th fractionation (F₄SKL) extraction were collected for further electrospinning and characterization.

2.2.2 Preparation of Lignin-based Carbon Nanofiber

The manufacture process of lignin carbon nanofiber shows in Fig. 3. Electrospinning solutions were prepared by dissolving F₄SKL:PEO with the 99:1 weight ratio in DMF. The solution was put in 80 °C oil bath for 2 hours, and then cooled to room temperature before electrospinning. Gauge number 25 needle was used (needle inner diameter 0.51mm) in combination with proper solution concentration (25–35 wt%). An electrospinning distance of 18 cm was used along with an applied voltage of 15 Kv at the 0.03 mL/min pump speed. A 5 °C/min heating rate to 250 °C for 60 minutes was used for thermo-stabilization in air atmosphere. For the carbonization process, a heating rate of 10 °C/min was used to heat the thermally stabilized lignin fibers to 800 °C, 900 °C, and 1000 °C ultimate heating temperature respectively for 60 minutes at each temperature in nitrogen atmosphere.

2.2.3 Preparation of Lignin-based Magnetic Composite Carbon Nanofiber

AAI was dissolved in DMF and then 35 wt% F₄SKL/PEO (99/1 w/w) was added to the AAI-DMF solution (AAI/lignin = 3 wt% or 10 wt%). The AAI-DMF-F₄SKL-PEO solution was heated to 80 °C for 2 hours, and then cooled to room temperature before electrospun into nanofiber mats. Stabilization of the as-spun fibers was performed by heating the fibers to 250 °C in air at a heating

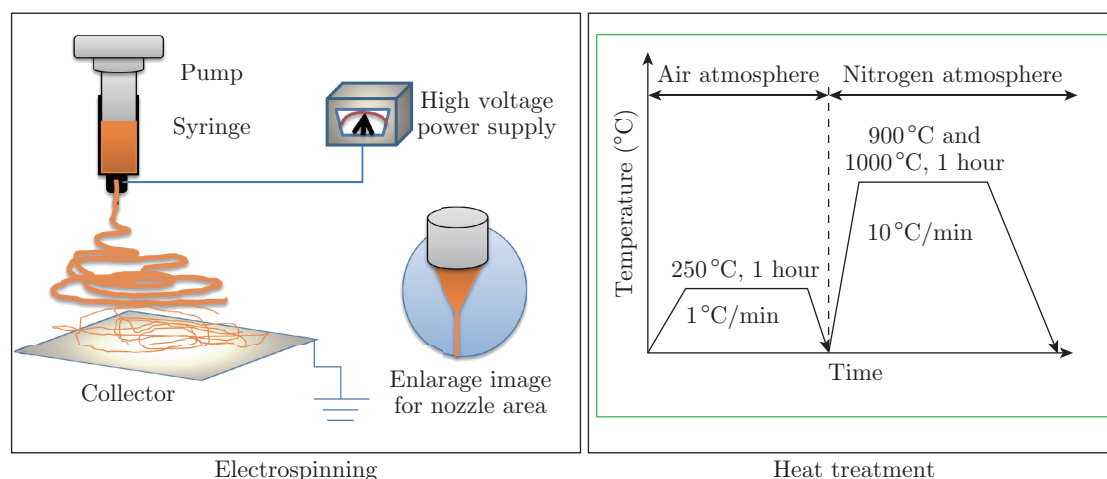


Fig. 3: Manufacture process of electrospun lignin carbon nanofiber

rate of 1 °C/min and held for 1 hour before cooling down to room temperature. Carbonization and the growth of magnetic iron oxide nanoparticles were achieved by treating the thermo-stabilized fibers at 10 °C/min to 900 °C and 1000 °C under Nitrogen and held at temperature for 1 hour.

2.2.4 Lignin Nanofiber Mats and Single As-spun Nanofiber Mechanical Properties Characterization

Mechanical properties of F₄SKL nanofiber mats were conducted using the KES-G1 Kawabata microtensile testing system at the elongation rate of 0.01 cm/s. For random nanofiber mats, sample strips of 4 cm×0.5 cm were glued on a paper frame for testing. The gauge length for tensile test was 3 cm. Single as-spun nanofiber mechanical testing were conducted using the *Nano Bionix*TM tensile testing system (*Agilent Technologies*). Nanofiber samples were first collected on a 5 mm gauge length plastic template during the electrospinning process. The Kleindiek nanomanipulator and Olympus LEXT OLS 4000 confocal microscope were used for nanofiber selection and removal until one single nanofiber remained on the template for testing.

2.2.5 Characterization of Lignin-based Magnetic Carbon Nanofiber and Its Composite

Composite nanofibers were characterized using scanning electron microscopy (SEM, Hitachi S-3000N), and transmission electron microscopy (TEM, Hitachi H7600). The two-point probe method was used to measure electrical conductivity. A Superconducting Quantum Interference Device (SQUID) was used to measure the magnetic hysteresis at 300 K.

3 Results and Discussion

3.1 Lignin Carbon Nanofiber for Structural Applications

Lignin-based carbon fiber production has several advantages over PAN and pitch-based carbon fibers. It is not only a low cost and high carbon content material but is an abundant renewable

resource. The high oxygen content of lignin will likely mean a shorter stabilization time and lower stabilization temperature compared to other precursors. Yet, the challenge remains preparing a consistent and uniform lignin substrate from such a complex and variable compound, including impurities and modifications during isolation, from industrial processes like Kraft pulping [1-6, 8, 11].

3.1.1 Carbon Fiber Performance Map

An examination of the carbon fiber performance map shows that the strength of lignin-based carbon fiber is about one-tenth of that of the commercial PAN-based carbon fiber (3-7 GPa) (Fig. 4). It is well known that the fiber strength could increase through the decrease of fiber diameter because of the reduction in size and quantity of defects as well as improvements in molecular orientation. Therefore, electrospinning technique has been utilized in this research as a means to generate nano-scale fibers to improve the strength and expand the application of lignin-based carbon fibers [15, 16].

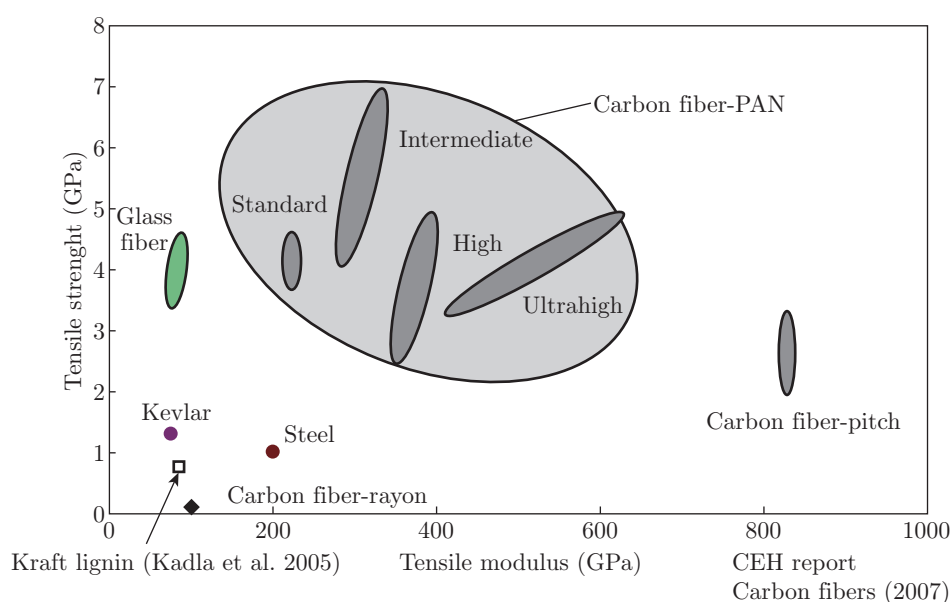


Fig. 4: Mechanical performance map of carbon fiber from different precursors [1]

3.1.2 Effect of Fiber Alignment and Heat Treatment

During the electrospinning process, the fibers were randomly distributed on the collector and formed random fiber mats. One method to enhance the electrospun nanofiber assembly strength is to use a rotating fiber take-up device, such as a rotating drum or wheel [10]. Rotating drum with high rotating speed can not only improve the fiber alignment in high rotation speed but also further stretch the electrospinning jet. Fibers with smaller diameters and higher degree of molecular orientation could be obtained, resulting in improved mechanical strength [15]. The representative SEM images of random and aligned as-spun and 1000 °C carbon nanofibers are shown in Fig. 5. The F₄SKL nanofibers were uniform and bead-less before and after heat treatment. The 1000 °C carbon nanofiber yield was 46.17% by weight. The average diameter of the as-spun randomly

distributed fibers was 667 ± 112 nm, while the average diameter of the thermo-stabilized and 1000 °C carbon nanofibers were 551 ± 91 nm and 474 ± 81 nm, respectively. The average fiber diameter of the as-spun, thermo-stabilized, and 1000 °C carbon aligned F₄SKL nanofibers were 499 ± 71 nm, 420 ± 60 nm, and 368 ± 62 nm, respectively. The fiber diameter of the aligned nanofibers was smaller than the randomly distributed nanofibers at the same conditions, which could be due to further stretching of fibers during electrospinning process [15, 20].

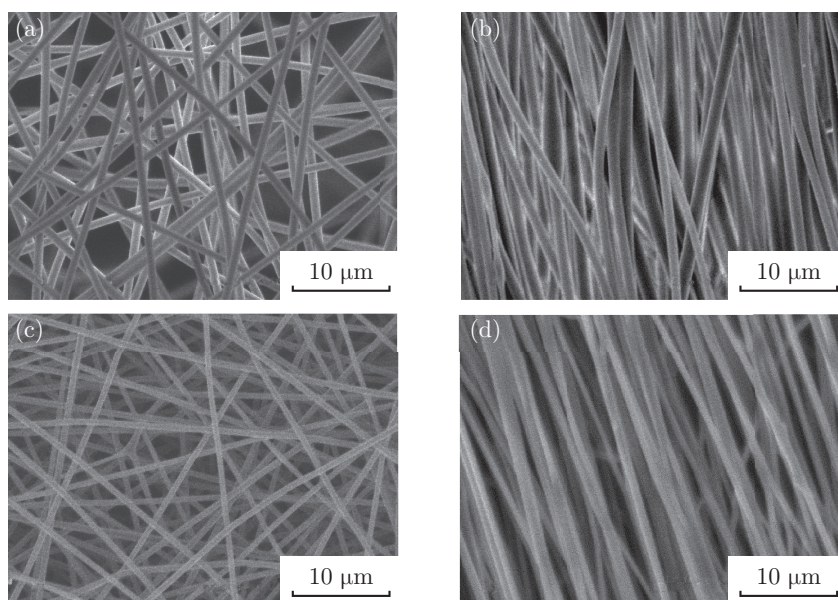


Fig. 5: Morphology of F₄SKL (a) Random as-spun, (b) Aligned as-spun, (c) Random carbon, and (d) Aligned carbon nanofibers

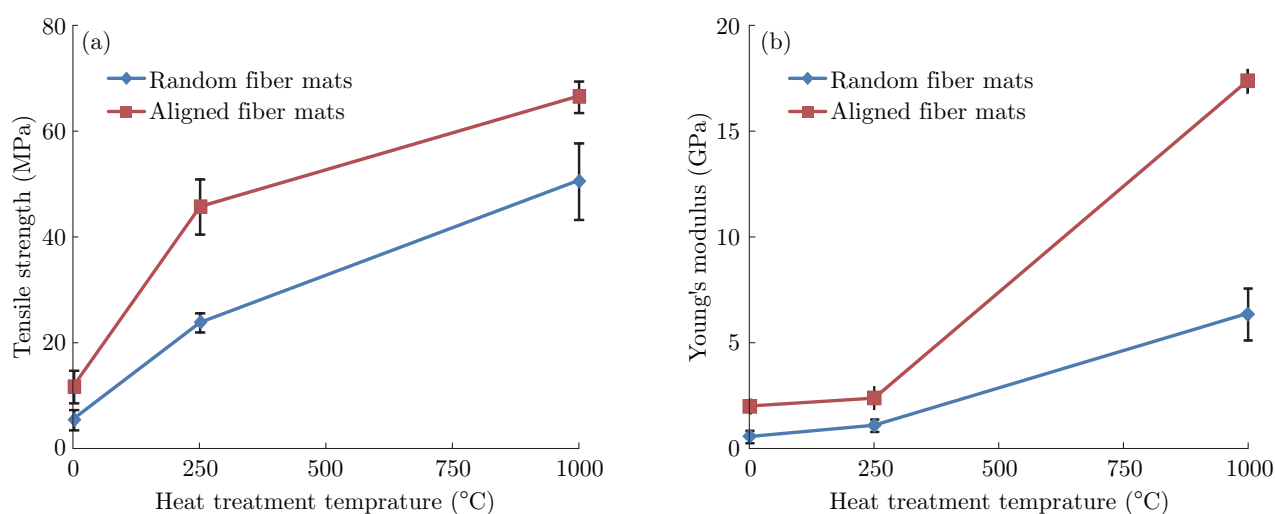


Fig. 6: Tensile strength (a) and Young's modulus (b) of F₄SKL random and aligned nanofiber mat

Fig. 6 shows the tensile strength and Young's modulus of F₄SKL random nanofiber mats and aligned nanofiber mats before and after carbonization. The results indicated that the strength of F₄SKL as-spun random fiber mats (5.5 MPa) was lower than that of the PAN as-spun random nanofiber mats (8.9 MPa) reported in previous research [28]. The tensile strength of the random

carbon nanofiber mat increased by an order of magnitude from 5.5 MPa to 50 MPa after carbonization at 1000 °C, whereas the aligned carbon nanofiber mats have six times increased from 11 MPa to 66 MPa. Young's modulus of 1000 °C random and aligned carbon nanofiber mats was 6.3 ± 1.23 GPa and 17.4 ± 0.6 GPa, respectively. The strain at break of random and aligned carbon nanofiber mats was $2.0 \pm 1.2\%$ and $0.8 \pm 0.2\%$, respectively. Comparing the 1000 °C random and aligned carbon nanofiber mats revealed that the tensile strength improved by 32%, while the Young's modulus improved by 175% after alignment.

3.1.3 Single As-spun Nanofiber Mechanical Properties and Effect of Single-walled Carbon Nanotube (SWNT) Reinforcement

Single nanofiber tensile tests were performed to characterize the mechanical properties of the lignin-based electrospun nanofibers and to translate single nanofiber mechanical properties to different nanofiber assemblies such as random and aligned nanofiber mats. The result of single nanofiber mechanical strength test showed that the average strength and Young's modulus of single F₄SKL as-spun nanofiber were 34.36 ± 11.53 MPa and 2.91 ± 1.34 GPa, respectively. Single as-spun nanofiber was around 5-8 times higher than that of the as-spun random nanofiber mat (Fig. 8). Strong materials such as carbon nanotubes (CNT) can be added to achieve fiber strength reinforcement for electrospun nanofibers. Previous research has shown that the Young's modulus of nanofiber could be increased three to four times by adding a small amount of CNT (1-5% w/w) [15-16]. To avoid the agglomeration of CNT, emulsion electrospinning was used to prepare uniform core-shell composite nanofibers [22, 24]. Core-shell composite nanofibers were prepared by electrospinning a water-in-oil emulsion wherein the aqueous phase consisted of single-walled carbon nanotubes (SWNT) in aqueous suspensions and the oily phase made use of the F₄SKL solution system with SpanTM 80 as surfactant. The resulting fiber morphology of the composite nanofibers is shown as Fig. 7. Single nanofiber tensile tests were also performed on F₄SKL/SWNTs composite as-spun fiber. 30 wt% F₄SKL/SWNTs (99.5/0.5 w/w) as-spun nanofibers were collected for single nanofiber tensile testing, and the average fiber diameter was 886 ± 248 nm. A representative stress-strain curve of single as-spun nanofiber and a random nanofiber mat is shown in Fig. 8. The average strength and Young's modulus of the 30 wt% F₄SKL/SWNTs as-spun nanofiber was 46.60 ± 7.84 MPa and 3.73 ± 0.52 GPa, respectively, which were higher than that of the pure F₄SKL as-spun nanofiber with strength and Young's modulus of 34.36 ± 11.53 MPa and 2.91 ± 1.34 GPa, respectively.

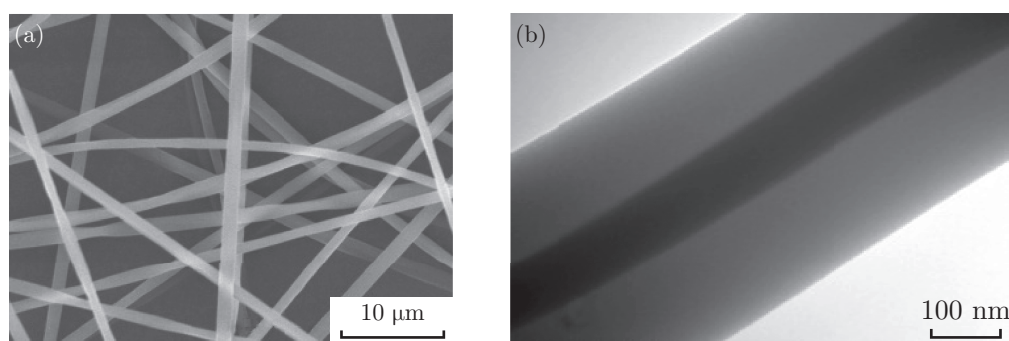


Fig. 7: (a) SEM image of 30 wt% SKL/SWNTs as-spun fiber in pure DMF solution system. (b) TEM images of as-spun fiber with core (SWNTs) and shell (SKL) structure

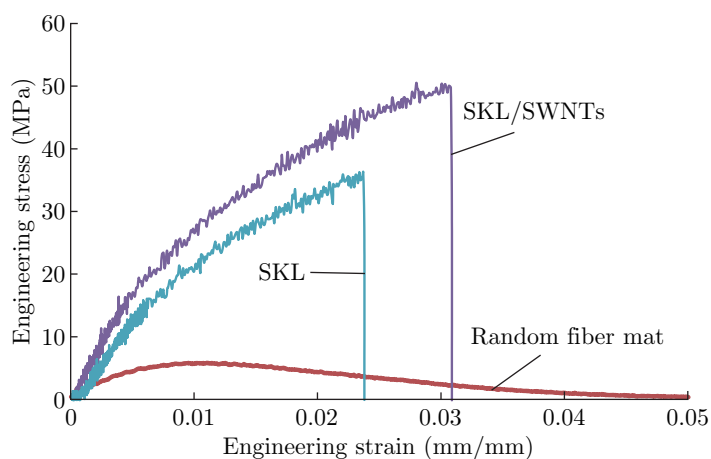


Fig. 8: Representative stress-strain curves of single as-spun SKL fiber, SKL/SWNTs fiber, and random fiber mat

3.2 Electromagnetic Lignin Carbon Nanofibers

To illustrate the concept of multifunctional composite nanofibers magnetic iron oxide nanoparticles were added to lignin to introduce magnetic properties by facile in-situ synthesize method [29–34]. These nanoparticles and their matrix lignin were processed by electrospinning and carbonization to prepare lignin-based composite carbon nanofibers. Fig. 9 shows the typical SEM image of lignin-based magnetic carbon nanofiber and TEM image of lignin-based magnetic carbon nanofiber. The carbonized fiber average diameter is 600 nm. Through carbonization of lignin composite nanofibers, electrical conductivity was introduced. The electrical conductivity of lignin carbon nanofiber mat was 2 ~5 S/cm that is comparable to that of PAN based carbon nanofibers [23, 33–34]. The magnetic properties ($M_s = 1.8 \sim 7.4$ emu/g, $M_r = 0.15 \sim 2.21$ emu/g and coercivity = 108~125 Oe) also found to be similar to that of PAN based magnetic carbon fibers [23, 33–34]. Fig. 10 displays the typical magnetic hysteresis loop of magnetic lignin carbon nanofiber. With the combination of magnetic permeable and electrically conductive functions, a new family of hybrid lignin composite nanofibers has been created with great potential to enable the formation of critical components for electromagnetic interference (EMI) shielding.

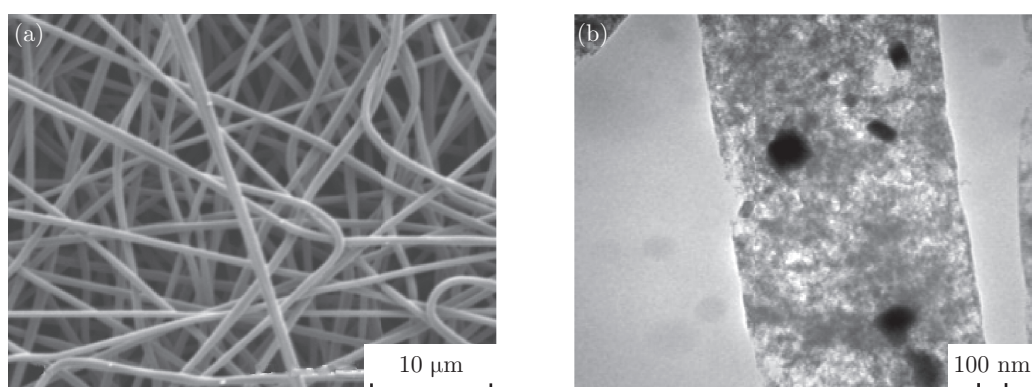


Fig. 9: Typical SEM image (a) of lignin-based magnetic carbon nanofiber and TEM image (b) of lignin based magnetic carbon nanofiber

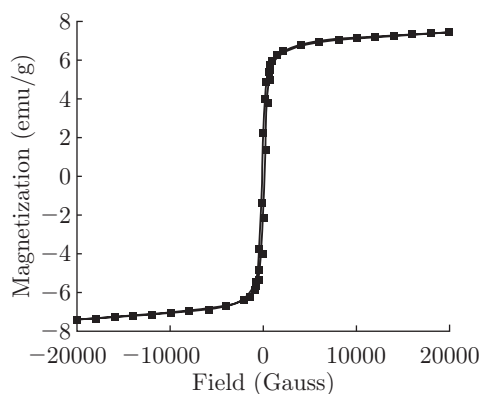


Fig. 10: Typical magnetic hysteresis loop of electromagnetic lignin carbon nanofiber

4 Conclusions

Lignin-based carbon nanofiber was prepared by electrospinning method. F₄SKL electrospun random and aligned nanofiber mats were fabricated in this research and then converted into carbon nanofiber mats. The mechanical strength of random nanofiber mats gained an order of magnitude increase from 5 MPa to 50 MPa after carbonization at 1000 °C, while the corresponding aligned carbon nanofiber mats further increased from 11 MPa to 66 MPa. The Young's modulus of 1000 °C random and aligned carbon nanofiber mats was 6.3 ± 1.23 GPa and 17.4 ± 0.6 GPa, respectively. These results indicated that fiber alignment could improve the tensile strength by 32% and Young's modulus by 175%. SWNT was added to form composite F₄SKL/SWNT nanofiber by emulsion electrospinning, and the single as-spun nanofiber tensile test result showed that the tensile strength and Young's modulus both increased comparing to the pure F₄SKL as-spun nanofiber.

Lignin-based carbon nanofibers with electromagnetic properties were produced. The electrical conductivity and magnetic properties of lignin-based nanofiber were found to be comparable or superior to that of PAN based magnetic carbon nanofibers. The encouraging results demonstrated the potential of lignin as an engineering material thus establishing a pathway for adding values to the abundantly available and renewable lignin.

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